

Express Mail No.: EV322400241US

UTILITY PATENT APPLICATION

of

TUCKER D. MAURER

for

METHODS FOR PASSIVATING STAINLESS STEEL

Attorney Docket No.: 14960-0012

## **METHODS FOR PASSIVATING STAINLESS STEEL**

### **Cross-Reference of Related Applications**

This application claims the benefit of U.S. Provisional Patent Application No.  
5 60/426,147 filed November 14, 2002, the disclosure of which is expressly  
incorporated herein by reference.

### **Field of the Invention**

10 The present invention relates generally to methods for passivating stainless  
steel, and more specifically to pickling and passivation of low chromium steel in the  
absence of nitric acid.

### **Background and Summary**

15 The industry standard for pickling stainless steel is to use a hot solution of  
nitric acid and hydrofluoric acid. Such pickling processes produce hydrofluoric acid  
vapors and waste nitrates that require special disposal procedures. Alternatives to such  
processes have been explored, including mechanical abrasion and electrolytic pickling  
20 methods. One alternative, disclosed in U.S. Patent No. 5,821,212, assigned to Crown  
Technology, Inc., to Peterson (Rinse Aid and Process for Stainless Steel) involves a  
peroxide-based rinse additive for cleaning stainless steel following pickling with more  
traditional mineral acids.

Numerous methods exist in industry and in the literature to improve stainless  
25 steel's inherent corrosion resistance through passivation, however most involve nitric  
acid and/or treatment with hexavalent chromium solutions. These options can be  
hazardous and lead to significant waste treatment costs. In response to growing  
environmental concerns, many have attempted to create passivation processes that do  
not involve nitric acid or hexavalent chromium. Citric acid based passivation

protocols have received a lot of positive attention. However, citric acid passivation has not achieved the desired results. Therefore, there has emerged a need for non-nitric acid passivation methods that are also effective in connection with non-nitric acid pickling methods.

5           The present invention includes methods for passivating stainless steel after pickling treatment in the absence of nitric acid. The methods include the steps of cleaning the pickled stainless steel with an alkaline composition to obtain clean steel, activating the clean steel with an activator composition to obtain activated steel, and passivating the activated steel with a passivating composition in the absence of nitric  
10 acid. In the preferred embodiment of this invention the activator composition contains at least one activator. The activator has a significantly higher binding affinity for iron than for chromium as evidenced by their metal complex formation constants.

Other features and advantages of the present invention will become readily apparent from the following detailed description, the appended claims and the  
15 accompanying drawings. It is to be understood that both the foregoing general description and the following detailed description are exemplary and provided for purposes of explanation only, and are not restrictive of the invention, as claimed.

**Brief Descriptions of Drawings**

Fig. 1 is a chart showing the Auger electron spectroscopy results for type 409 stainless steel treated according to this invention.

5        Fig. 2 is a chart showing the Auger electron spectroscopy results for type 409 stainless steel treated with a molybdenum passivator according to this invention.

Although the drawings represent embodiments of the present invention, the drawings are not necessarily to scale and certain features may be exaggerated in order to better illustrate and explain the present invention. The exemplification set out  
10    herein illustrates certain embodiments of the invention, in one or more forms, and such exemplifications are not to be construed as limiting the scope of the invention in any manner.

**Detailed Description of Preferred Embodiments**

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and examples and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. The invention includes any alterations and further modifications in the described compositions and methods and further applications of the principles of the invention that would normally occur to one skilled in the art to which the invention relates.

The present invention provides processes for treating stainless steel in the absence of nitric acid. The processes are environmentally friendly, efficient, quick, effective and affordable. One advantage of the methods of the present invention is that they allow the use of low chromium steel such as type 409 steel in place of more costly higher chromium stainless steel materials. Moreover, using the methods of the present invention, low chromium stainless steel can be treated to achieve a high chromium/iron ratio that is comparable to the oxide layers of higher chromium, more expensive materials that have been treated using nitric acid. The methods of the present invention are effective to reduce surface impurities, such as titanium and aluminum, and improve corrosion protection.

In one particular embodiment, the invention provides a three-step immersion process including a cleaning step, an activation step, and a passivation step. In other embodiments, the three-step process can be accomplished by spraying instead of immersion.

According to one embodiment of the present invention, stainless steel is first pickled using methods known in the art to obtain pickled stainless steel. In some

pickling methods, the stainless steel is acid pickled in the absence of nitric acid. In some embodiments, the stainless steel is descaled. A composition and method is disclosed in U.S. Patent No. 5,821,212, assigned to Crown Technology, Inc., the disclosure of which is herein expressly incorporated by reference.

5           After pickling, the steel may be processed by annealing, cold rolling, temper rolling, formed into sheets or other objects, or other post-pickling processes. After such processes, the steel may be passivated.

          The methods of this invention include cleaning the pickled stainless steel with a basic composition to obtain cleaned steel. The basic composition may include an  
10   alkaline cleaner with various anionic, non-ionic, cationic and amphoteric surfactants for removing mill dirt, oils, grease and other soil. The cleaning step can be important because such soils may prevent passivation.

          In some embodiments, the steel is also electrolytically cleaned using methods known in the art. Electrolytic cleaning removes alloyed impurities up to several atom  
15   layers deep. This step is desirable in mills that produce titanium carbide inclusions or other impurities on the surface of the stainless steel. Such inclusions can render the steel unpassivable. In addition, electrolysis smoothes and brightens the surface. Inclusions may also be removed by chemical etching, but produces a product with inferior surface quality and is less aesthetically pleasing.

20           The clean stainless steel is then treated with an activator composition. The purpose of the activator is to enrich the chromium content through selective reaction of the iron from the solid steel matrix and prevent its redeposition into the passive layer. The activator for the activator solution is selected from a group of organic and inorganic compounds that form iron complexes with particularly high formation  
25   constants relative to their chromium analogs. Other criteria for selecting compounds

for the activator solution include the water solubility of the ligand, the water solubility of the complex and cost of the compounds.

The present invention contemplates both organic and inorganic activators, however more organic compounds fit the above criteria. In some cases the activator is an organic chelator compound, such as carboxylic acids. Examples of carboxylic acids that are useful include oxalic, tartaric, gluconic, malic, and citric acids, as well as their water-soluble salts. The invention contemplates any carboxylic acid that satisfies the aforementioned selection criteria. The invention benefits from maximizing the complexing agent concentrations, and the concentration limit for these carboxylic acid chelators is dependent only on solubility. Common chelators such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) can also be utilized, however they tend to be less effective than carboxylic acids since they also bind chromium rather strongly.

The pH of the activator composition is selected based on the characteristics of the activator and is chosen to maximize the binding affinity. The organic activators are known to bind iron more strongly at higher pHs (i.e. in their anionic, not acidic form). By working at higher pH's, a greater percentage of the molecules are neutralized in solution to their anionic form, i.e. one drives the neutralization reaction to the right, toward completion.

In other embodiments, the activator is inorganic. Fluoride is a desirable activator because it is known to selectively dissolve iron from stainless steel substrates. Fluoride is an effective activator in both alkaline and acidic media, but an acidic pH tends to be more desirable.

The methods of this invention also include passivating the activated stainless steel. Passivation is defined as the chromium/iron ratio in the surface oxide layer of

the stainless steel. Higher chromium/iron ratios imply better passivation, which translates to better corrosion resistance.

The passivator section is a blend of oxidizing and phosphating technologies. In one embodiment, the passivation composition is phosphoric acid based with sodium fluoride and a ferrous/ferric iron "redox buffer" to maintain the electrochemical potential within the passive zone of the anodic polarization curve, characteristic of the stainless alloy (typically between 500-600mV vs. Silver/Silver Chloride (Ag/AgCl)). The redox potential of the bath can be maintained by any suitable oxidizer, however hydrogen peroxide is preferred due to environmental and cost considerations. The pH is another important factor, and can maintain by small additions of phosphoric acid. The optimal working pH is approximately 2.0-2.3.

As an acidic mixture, the fluoride in the bath activates, or "creates a chemically reactive surface" on the steel. Fluoride is thought to selectively dissolve iron from stainless steel surfaces, thereby improving the Chromium/Iron (Cr/Fe) ratio. In addition, as the acid in the mixture reacts with the steel, a small pH gradient is formed away from the surface. The pH is slightly higher at the surface of the steel, causing some insoluble phosphates to bond with surface, effectively building the oxide layer and providing additional corrosion protection. Furthermore, since the bath is redox controlled in the passive zone of the anodic polarization curve, significant metal losses are never realized because the surface will immediately oxidize, or passivate.

In one embodiment, the passivation bath includes about 25 g/L 85% w/w ("weight-to-weight") O-phosphoric acid, 10 g/L sodium fluoride, 2.45 g/L 50% w/w hydrogen peroxide, and 2 g/L dissolved iron. The source of iron can be from any



number of iron salts, but most preferably ferrous chloride. Other iron sources include, but are not limited to, ferric chloride, ferrous sulfate, and ferrous gluconate.

In still another embodiment, the invention provides a molybdenum passivator that provides superior results in the absence of nitric acid. The molybdenum passivator can be used with both organic and inorganic activators. Due to the similarities in aqueous chemistry between chromium and molybdenum, it is believed that enhanced molybdenum to iron ratios can also impart improved corrosion resistance. This is further supported by the fact that stainless steel alloyed with molybdenum is known to be more corrosion resistant. Furthermore, molybdenum does not possess the high toxicity characteristic of chromium and is therefore safer to handle. In one embodiment, the passivation bath includes about 25 g/L 85% w/w phosphoric acid, 5 g/L sodium molybdate dihydrate, 5.0 g/L sodium fluoride, and 1.0 mL 50% w/w hydrogen peroxide.

The activation and passivation sections are designed to create maximum passivity. With maximizing the Cr/Fe ratio in mind, this can be achieved by selectively attacking the iron and enriching the chromium on the steel surface. Since chromium (II) oxide is known to be more inert to mineral acids than iron oxides, it was speculated that a dilute acid dip might selectively dissolve iron from the surface and improve corrosion resistance. Perhaps due to the incorporation of corrosive anions (i.e.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.) into the passive layer, this did not turn out to be the case. Use of these acids lead, in almost all cases, to accelerated corrosion. There seems to be a difference of opinion in the literature regarding the effects of these anions on corrosion resistance, but the salt spray results that were obtained were quite clear. Interestingly, a phosphoric acid/hydrofluoric acid combination seems to be an exception.

The following examples are provided to illustrate the present invention but are not intended to limit the reasonable scope thereof.

### EXAMPLES

5 In one experiment, described below, the cleaning bath was formulated with a surfactant, Miranol JEM 50 g/L (0.98 pounds per gallon) and 50 g/L 50% w/w caustic soda. The activator bath was prepared with 21.5 g/L oxalic acid dihydrate and 2 g/L 50% w/w caustic soda. The passivation bath was formulated with 25 g/L 85% w/w phosphoric acid and 11 g/L sodium fluoride, 7.1 g/L ferrous chloride tetrahydrate and  
10 2.45 g/L 50% w/w hydrogen peroxide. In another experiment, described below, the ferrous chloride was substituted with 9.93 g/L ferrous sulfate heptahydrate. In both cases the balance was water.

#### Example 1: Comparison to Nitric Acid Pickled High Chromium Steel.

A single lot of type S40900 stainless steel was obtained from a stainless steel  
15 manufacturer and cut into 3" x 6" coupons for passivation tests. The coupons were identified as Series 1, 2 and 3. The manufacturer was chosen because its method of processing does not involve nitric acid and therefore has limited natural passive qualities. The alloy was chosen because it has the lowest chromium content and hence possesses the least natural corrosion resistance of all the stainless steel alloys.

20 A single lot of type S40900 stainless steel, which was pickled with a nitric acid solution, was obtained from another stainless steel manufacturer and cut into 3" x 6" coupons. The coupons were identified as Series 4.

Passivation baths were prepared as follows:

25 Bath 1 (cleaner):	50% w/w Caustic Soda .....	50 g/L
	34% w/w Amphoteric surfactant .....	50 g/L
Bath 2 (activator):	Oxalic acid dihydrate .....	21.8 g/L
	50% w/w Caustic Soda .....	2.0 g/L (pH = 10.5 - 11.5)

Bath 3 (passivator): 85% w/w Phosphoric Acid ..... 25 g/L  
 Sodium Fluoride ..... 11 g/L  
 Ferrous Chloride Tetrahydrate ..... 7.1 g/L  
 50% w/w Hydrogen Peroxide, dropwise →  $E > 500 - 600$  mV vs.  
 Ag/AgCl reference electrode. (pH = 2.0 - 2.3, optimally)

A nitric acid passivation control bath was prepared according to ASTM  
 method A-380 for this series stainless steel:

Bath 4 (Control): Concentrated Nitric Acid ..... 250 g/L  
 Sodium Dichromate Dihydrate..... 50 g/L

Baths 1 and 2 were heated on a hot plate to 140°F, while bath 3 was  
 maintained at ambient temperature. While the operating temperatures of baths 1 and 2  
 are non-critical, the temperature of bath 3 cannot exceed 120°F without precipitation  
 occurring. The nitric acid/hexavalent chrome control bath (4) was heated and  
 maintained at 120° to 140° F.

The stainless steel coupons were then subjected to a passivation treatment of  
 this invention by immersion in baths 1, 2 and 3 for various periods of time. Similarly,  
 control samples were exposed to passivation treatments as described in method  
 ASTM A-380 through immersion in baths 1 and 4. The degree of  
 passivation/corrosion protection was then evaluated via ASTM method B117 salt  
 spray exposure. The coupons were examined and rated relative to one another. The  
 results are listed in Table 1 below.

**Table 1: Passivation Results**

Coupons	Bath 1 Immersion (cleaner)	Bath 2 Immersion (activator)	Bath 3 Immersion (passivator)	Bath 4 Immersion (control)	Salt Spray Results
Series 1A	5 min	5 min	5 min	-	excellent
Series 2A	5 min	-	5 min	-	average
Series 3A	5 min	5 min	-	-	poor
Series 4A	5 min	1 min	1 min	-	v. good
Series 1B	5 min	-	-	15 min	v. good
Series 2B	5 min	-	-	30 min	excellent
Series 3					v. poor

(untreated)					
Series 4 (nitric pickled)					good

As the results in Table 1 demonstrate, the salt spray corrosion resistance imparted by the passivation treatment of this invention matches or exceeds that of the nitric acid/hexavalent chrome treatment, but at considerably shorter immersion times and without the hazardous constituents. It should also be noted that duplicate samples were subjected to humidity chamber corrosion tests (100% humidity, 95°F) with identical results.

The results for this experiment are presented as relative values because the experiments were conducted using accelerated corrosion chambers (i.e. salt spray, copper accelerated acetic acid spray, humidity, etc.). Using such chambers, results can vary between runs and do not directly correlate to corrosion in real life applications. Therefore, such results are useful to the extent they are compared to results from the same salt spray test run. In addition, the results obtained from one chamber to the next (even when trying to meticulously duplicate the parameters) are rarely equivalent, again except in relation to other processes; i.e. a superior process in one chamber should be superior in all chambers. Due to the relative nature of these results, Auger analyses of the processes were performed as described in the next example.

#### Example 2: Spectroscopy Analysis

In an effort to quantify the extent of passivation afforded by the processes of this invention, samples of the coupons from Example 1 were subjected to Auger electron spectroscopy analysis to determine the chromium to iron ratios in the surface oxide layer. The Auger electron spectroscopy chart is shown in Fig. 1. As expected, the analysis yielded enriched chromium levels in the oxide layer, and chromium to iron ratios of greater than one on samples that were process treated for periods of at

least one minute. In addition, the results showed that the enrichment increased as a function of treatment time, suggesting that improved corrosion protection could be realized from extended immersion times. Table 2 summarizes the typical results obtained from Auger analysis of passivation process treated samples, as well as the average passivation obtained from the ASTM A-380 treatment (described above) and the common nitric acid pickling process.

**Table 2: Surface Oxide Characteristics**

<b>Process</b>	<b>Cr/Fe Ratio (surface)</b>	<b>Cr/Fe Ratio (<math>O_{max}</math>)</b>	<b>Passivation Depth (Cr/Fe <math>\approx</math> 1)</b>	<b>Cr Enrichment Depth</b>	<b>Oxide Thickness</b>
<b>5 minute Passivation (series 1A)</b>	1.46	1.14	149 Å	> 1600 Å	900 Å
<b>1 minute Passivation (series 4A)</b>	1.24	1.05	36 Å	362 Å	95 Å
<b>ASTM A-380 Passivation (series 2B)</b>	1.3	N/A	13 Å	26° Å	N/A
<b>Nitric Pickled (series 4)</b>	0.51	0.45	-	45 Å	71 Å

As the Auger spectroscopy results indicate, the passivation process of this invention imparts several corrosion resistant properties to this low chromium alloy. First, and most importantly, the chrome to iron ratios are significantly higher than the non-treated panels as well as their nitric acid pickled analogs. In addition, the corrosion performance is further augmented by the improved passivation depth (the depth at which the chrome and iron levels begin to diverge quickly to their base metal compositions) and chromium enrichment depth (the depth at which the chromium level remains higher than the base metal chromium composition). These characteristics are important to the sample's ability to resist corrosion following a scratch or an abrasion.

Example 3: Effect of Concentration Differences.

To determine the efficacy of the passivation bath (Bath 3) during periods of concentration fluctuations, a series of baths were prepared to simulate lean and rich conditions and evaluated versus the passivation treatment described previously. The results are shown in Table 3 below.

**Table 3:Concentration-Determined Performance Trends**

<b>Perturbation</b>	<b>Trend</b>	<b>Reason</b>
2X Phosphoric Acid	Moderately negative	Interference color patterns
½ Phosphoric Acid	Slightly negative	Corrosion performance
No Sodium Fluoride	Slightly negative	Corrosion performance
½ Sodium Fluoride	Slightly negative	Corrosion performance
2X Sodium Fluoride	Highly negative	stability issue (pH)
Redox potential < 500 mV	Slightly negative	Corrosion performance
Redox potential > 600 mV	Moderately negative	Corrosion performance
Ferrous Sulfate	None	Equivalent corrosion performance Slightly inferior bath life

It is important to note that the importance of the iron to the passivation process is to act as a redox buffer. The hydrogen peroxide addition oxidizes ferrous iron to ferric iron, which helps maintain the redox potential of the passivation bath at 500 to 600 mV vs. the Ag/AgCl reference electrode. As more stainless steel is processed, ferrous iron builds in the passivator bath and lowers the redox potential. The redox potential of the bath can be easily monitored using an ORP probe that is set to trigger the addition of small volumes of hydrogen peroxide that oxidizes the ferrous iron to ferric. In this way the redox potential of the passivation bath can be maintained in the optimal range.

#### Example 4: Preparation of Fluoride Activators

An activator composition containing the following was prepared: 25 g/L 85% w/w phosphoric acid; 10 g/L sodium fluoride at pH = 2.56. A second activator solution containing the following was prepared: 21.8 g/L oxalic acid dihydrate; 10 g/L sodium fluoride with 50% w/w caustic soda added dropwise to a pH of about 10-11. Activator baths were prepared, which contained the activator compositions of this Example.

Stainless steel coupons were treated using the activator baths of this Example with Baths 1 and 3 as described in Example 2. Salt spray tests showed excellent results.

#### Example 5: Comparison of Activators

Several organic and inorganic activators were compared using the processes of Example 1. An alkaline bath without any activator was also used as a control. The relative performance results in Table 4 show that the superior results of this invention are due to the activators of this invention and not merely the alkaline pH of the activator bath.

The fluoride activators of Example 3 were also used in the processes of this invention. The performance results are compared in Table 4. The fluoride activators of this invention perform better when the second bath is maintained at acidic pH, but good results are also obtained at alkaline pH.

The process of Example 1 using baths 1, 2, and 3 were performed using the common chelating agents shown below in Table 4 in place of oxalic acid. The fluoride activators described in Example 3 were also compared. The results are shown in Table 4.

**TABLE 4 - COMPARISON OF ACTIVATOR PERFORMANCE**

<b>ACTIVATOR</b>	<b>pH</b>	<b>RELATIVE PERFORMANCE</b>
Oxalic Acid	> 10	Excellent
Tartaric Acid	> 10	Excellent
Citric Acid	> 10	Excellent
Alkaline Bath without Activator	> 10	Poor
Fluoride	2-3	Excellent
Fluoride	>10	Very Good
Fluoride	2.56	Excellent
Fluoride	10 to 11	Very Good
Ethylenediaamine Tetracetic Acid	> 10	Good
Nitrilotriacetic Acid	> 10	Good

Example 6: Spectroscopy Analyses

5

Series 1A and Series 4A Coupons from Example 1 were subjected to Auger Electron Spectroscopy Analysis. Values such as chromium to iron ratio, passivation depth, chromium enrichment depth and oxide thickness were compared to the same values for other processes. The results are shown in Table 5.

10

Process A relates to the best results published in the literature for nitric acid process, performed with high chromium stainless steel.

Process B is a non-nitric acid pickling treatment on low chromium steel without passivation.

15

Process C is low chromium stainless passivated ala ASTM A-380.

Process D is nitric acid pickled/passivated low chromium steel.

20

Processes E and F are non-nitric acid pickled low chromium stainless steel, passivated according to the invention for periods of one-minute (E) and five minutes (F).



**TABLE 5: PROCESS COMPARISONS**

	Process	Cr/Fe Ratio (max)	Cr/Fe Ratio (at Omax)	Passivation Depth (Cr/Fe $\approx$ 1)	Cr Enrichment Depth	Oxide Thickness
A	High Cr "Best" Published Process	1.75	N/A	20 Å	-	N/A
B	Low Cr non-Nitric Acid treatment	0.30	0.30	-	-	65 Å
C	ASTM A-380	1.3	N/A	13 Å		N/A
D	Nitric Pickled (industrial)	0.51	0.45	-	45 Å	71 Å
E	Low Cr 5 minute Passivation	1.46	1.14	149 Å	>1600 Å	900 Å
F	Low Cr 1 minute Passivation	1.24	1.05	36 Å	362 Å	95 Å

**Example 7: Molybdenum Passivator**

5

The protocol of Experiment 1 was repeated with the following baths:

- Bath 1 (cleaner): 50% w/w Caustic Soda ..... 50 g/L  
34% w/w Amphoteric surfactant ..... 50 g/L
- 10 Bath 2 (activator): 85% Phosphoric acid ..... 25 g/L  
Sodium fluoride ..... 10 g/L  
at pH = 2.56.
- 15 Bath 3 (passivator): 85% Phosphoric Acid ..... 25 g/L  
Sodium Fluoride ..... 5 g/L  
Sodium molybdate ..... 5 g/L  
50% w/w Hydrogen Peroxide ..... 1.0 mL  
→  $E > 640$  mV vs. Ag/AgCl reference electrode  
20 at pH = 1.7.

The use of the molybdenum passivator yielded superior results. The salt spray performance of the molybdenum passivated samples was superior to the prior art treated samples. Samples were also subjected to Auger electron spectroscopy analysis

to determine the molybdenum to iron ratios in the surface oxide layer. The analysis yielded enriched molybdenum levels in the oxide layer, and molybdenum to iron ratios of greater than nine on samples that were process treated for periods of at least two minutes. The Auger electron spectroscopy chart is shown in Figure 2.

5           Passivation, or chromium/iron ratio, values for the 5-minute immersion of the present invention compares very favorably to the prior art processes A through D. Typically a chromium/iron ratio of 1 or greater is desirable, particularly for low chromium stainless steel. Moreover, the passivation depth for the 5-minute immersion process of the present invention is far superior to the best process reported in the  
10 literature, which was performed on a HIGH chromium stainless steel alloy.

The results of these experiments show that the methods of this invention achieve results with non-nitric acid treated low chromium stainless steel that is equal to or superior to prior art processes.

Other embodiments of the invention will be apparent to those skilled in the art  
15 from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification, drawings and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims. It should be understood that only the preferred embodiments have been shown and described and that all changes and modifications that come within the  
20 spirit of the invention are desired to be protected.